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主 論 文 の 要 旨

論文題目　**Development of Highly Corrosion Resistant Platings via Structure Design (構造制御による高耐食性めっきの開発)**

氏　　名　**PARK　Jaehyeok**

論 文 内 容 の 要 旨

Corrosion is a natural and inevitable phenomenon that has become a big concern in the modern society. Corrosion proceeds inconspicuously and slowly and causes deformation and deterioration of metal materials. For example, the corrosion of structure materials has led to deterioration and breakdowns of social infrastructure facilities such as bridges, buildings and causes enormous maintenance cost, even damage to human life. Corrosion is also a common problem close to human daily life. Corrosion is problematic in automobile and aircraft components, metal tools, electronic devices, and home appliances and so on. Thus, corrosion protection is one of the major tasks of recent times and the corrosion resistance of metal materials is considered as a most fundamental and essential property. Moreover, recently developed and future technologies are also closely related to corrosion protection technologies. Various technologies in areas, such as clean energy production and environmental conservation are being developed to reach the global goals for sustainable development. Many of these technologies required advanced, safe and environmental-friendly corrosion protection technologies. For example, polymer electrolyte fuel cell (PEMFC), which is expected to be one of the most promising power sources using the environmental-friendly hydrogen as a fuel, high corrosion resistive components that can withstand the severe acidic environment during operation are essential. Therefore, the development of an advanced but safe and environmental-friendly corrosion protection technology is a long and ever-lasting desire for human being.

Among various surface treatment methods to prevent corrosion, plating has been widely used due to various advantages such as excellent performance and relatively low production cost. However, considering the fact that materials are becoming to be applied in applications subjected to more harsh corrosive environments than before and many conventional anti-corrosion plating contains toxic elements such as Cr^{6+}, Ni and Cd, increasing requirements for alternative plating with high corrosion resistance using harmless and abundant elements has drastically arose in recent years. Therefore, the development of an advanced but safe and environmental-friendly corrosion protection plating technology is essential not only provides solutions to problems of conventional technologies but also those of technologies to be developed in the future.

In this dissertation, as a possible method to improve the corrosion resistance of plating, 'structure design' of the plating is proposed. This dissertation summarizes a series of research on structure design of newly developed platings for improving the corrosion resistance of materials in various applications. Structure designs to meet requirements according to the applied environment and purpose are of great importance considering the diverse applications existing in the present and future society. The research aims to provide solutions for developing plating structures to improve properties than conventional plating and also to replace the existing plating using harmful elements. The developed structural design shall contribute to the development of the industry as well as realizing a sustainable future. Three approaches for structure design of platings have been explored considering the environment of three applications in this dissertation. Adapted methods are as follows:

I. Incorporation of functional carbon material into plating:
'Electrodeposition of metal/carbon composite plating'
II. The addition of the third element into binary alloy plating system:
'Electrodeposition of ternary alloy plating'
III. Stacking of an additional coating on top of the underlying plating:
'Electrodeposition of multilayer structured coatings'

Chapter 1 introduces the background of this research and the overall objective of this dissertation. The problems of corrosion and how essential it is to provide solutions against corrosion problems is explained taking current and future technologies issues of the world as an example. In addition, the approach of this research is explained by providing information on conventional knowledge and technologies. Furthermore, the objective of this research is clarified.

Chapter 2 deals with the structure control of coatings for the PEMFC, which is one of the most important future energy technologies that requires corrosion resistance. The applicability of metal/carbon material composite plating as a coating for PEMFC bipolar plate is considered, which requires not only high corrosion resistance but also electric conductivity in acidic environment. The incorporation of inert but conductive carbon nanotube (CNT) into Ni-W alloy plating structure had a positive effect on improving the corrosion resistance and lowering the contact resistance. The present of inert CNT onto the plating surface lowered the corrosion current density (I_{corr}) from 76.13 to 40.78 $\mu A \cdot cm^{-2}$ at 0.5M H_2SO_4 solution, which contributed to the improvement the corrosion resistance of the plating. In addition, CNT penetrated the surface oxide film on the Ni-W plating and lowered the contact resistance of plating from an average of 117.5 to 83.6 $m\Omega \cdot cm^2$ by acting as a conductive pathway. The change of the Ni-W plating structure by incorporating CNT into plating layer was effective for improving the corrosion resistance and conductivity of the Ni-W plating. Incorporation of inert and conductive CNT into the plating matrix was found to be an effective structure to realize required properties for PEMFC bipolar plate coatings.

Chapter 3 worked on the structure control of safe coatings to replace conventional hexavalent Cr plating. Electrodeposition of a novel ternary Fe-W-Zn alloy plating prepared by alloying of Zn into safe Fe-W platings is discussed as a possible candidate. It has been suggested that the corrosion resistance of binary Fe-W alloy can be improved by structure control of binary Fe-W plating via the addition of the third element; Zn, even though Zn is a base metal. The corrosion resistance of ternary alloy plating highly depends on the Zn content of ternary alloys, which is the main factor for determining the plating structure, intensively refining the grain size of the alloys. Nanocrystalline structured ternary alloys containing only about 1 to 2 at.% Zn showed improved corrosion resistance than binary Fe-W, Ni-W alloy and even Cr plating in 1M H_2SO_4 solution. The electrodeposited novel ternary Fe-W-Zn alloy structured by alloying of Zn into Fe-W alloys is expected to be a promising alternative to hexavalent Cr plating, without using harmful elements.

Chapter 4 reports the structure control of coatings to replace Zn-Ni platings, which are essential in the automotive industry. The corrosion resistance of electrodeposited ternary Zn-Fe-Mo plating was improved by lamination of an additional Mo oxide coating and its possibility as an alternative is discussed. Additional electrodeposition of about 300 nm thickness of Mo-oxide coating drastically improved the corrosion resistance of Zn-Fe-Mo plating. In the Mo oxide-coated Zn-Fe-Mo, initial red rust occurred after 60 cycles in the cyclic corrosion test (CCT), showed about 10 times improved corrosion resistance compared to the conventional Zn-Fe-Mo plating. The formation of multi-layer structure by lamination of an additional Mo-oxide coating on Zn-Fe-Mo plating had a critical effect on the enhancement of corrosion resistance by stabilizing protective Zn corrosion product, $Zn_5(OH)_8Cl_2{\cdot}H_2O$ (simonkolleite) phase. The formation of a multi-layer was proven to be an effective structure in improving the corrosion resistance.

Chapter 5 summarizes the finding and conclusion of this dissertation. As an overall conclusion, it was clarified that the corrosion resistance of the plating material can be significantly improved by appropriately designing the structure of the plating according to the applied environment and purpose. Even a small amount of additive, such as CNT and third elements, were found to drastically change the plating structure and their properties. In addition, structure design of platings can provide effective solutions for improving the properties of conventional platings and for replacing the existing platings which using harmful elements to harmless one. The developed structural design can contribute to the development of the industry as well as realizing a sustainable future society.